

Investigation of pressure-induced amorphization in hydrated zeolite Li-A and Na-A using synchrotron X-ray diffraction

M.D. Rutter^a, T. Uchida^b, R.A. Secco^{a,*}, Y. Huang^c, Y. Wang^b

^a*Department of Earth Sciences, University of Western Ontario, London, Ontario, Canada N6A 5B7*

^b*Consortium for Advanced Radiation Sources, The University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637, USA*

^c*Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7*

Received 27 June 2000; accepted 31 July 2000

Abstract

High pressure synchrotron X-ray diffraction measurements of hydrated zeolite Li-A and Na-A were carried out at pressures up to 4.1 GPa and at room temperature in a large volume press. Energy dispersive X-ray diffraction measurements showed progressive pressure-induced amorphization of both Li-A and Na-A samples. The most rapid loss in long-range ordering occurred at pressures up to 2.2 GPa followed by a gradual, continued decrease in ordering up to the maximum pressure. At 4.1 GPa the samples appeared to be X-ray amorphous. After decompression, diffraction patterns at 1 atm indicated that the sample reverted back to their initial crystal structure. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: A. Amorphous materials; A. Microporous materials; C. High pressure; C. X-ray diffraction; D. Crystal structure

1. Introduction

Zeolites are aluminosilicates with well-developed microporous structures which have allowed them to be used extensively as molecular sieves, sorbents and as catalysts in the petroleum industry. The zeolites used in this study (Linde A) consist of an anion framework of silicon and aluminum (Si:Al, ratio 1:1) tetrahedrally bonded to oxygen with Li⁺ or Na⁺ providing charge balance [1]. The TO₄ (T = Si, Al) tetrahedra are linked together to form a three-dimensional framework of interconnecting pore and channel structures which may contain water of hydration. Due to their wide range of uses, their physical properties have been extensively studied at ambient pressure [2], however, there is only a hand full of studies examining the properties of zeolites under high pressure. Previous high pressure studies have indicated that some zeolites undergo pressure-induced amorphization [3–6]. Since its initial discovery [7], pressure-induced amorphization has received a great deal of attention [8,9] and the phenomenon has been observed in several materials [10–12]. Huang [3], reported

in an infra-red (IR) spectroscopic study that in addition to the pressure-induced amorphization of Li-A zeolites, at a pressure of 1.8 GPa, there was evidence that Li-A zeolite reverts back to its original structure upon decompression. However, no study has been conducted to examine the long-range ordering of Linde A zeolites under high pressure, or their reversion back to the ordered state upon decompression. Recently, the electrical properties of Linde A zeolites have been studied as a function of pressure [5,13] and an anomalous increase in ionic conductivity with pressure up to 1.7–2.2 GPa was observed in Li-A, Na-A and K-A zeolites. Therefore, in a broader context, knowledge of the structure of zeolites under pressure provides the grounds upon which the electrical properties can be interpreted. The purpose of this study is to examine the possible pressure-induced amorphization of zeolite Li-A and Na-A at room temperature and their structural memory characteristics using fixed angle synchrotron X-ray diffraction.

2. Experimental

Zeolite Na-A (Si/Al = 1) was synthesized hydrothermally from a mixture of 2SiO₂:Al₂O₃:5Na₂O:15H₂O heated at 80°C for 6 h. Li-A was prepared through conventional

* Corresponding author. Tel.: +1-519-661-4079; fax: +1-519-661-3198.

E-mail address: secco@julian.uwo.ca (R.A. Secco).

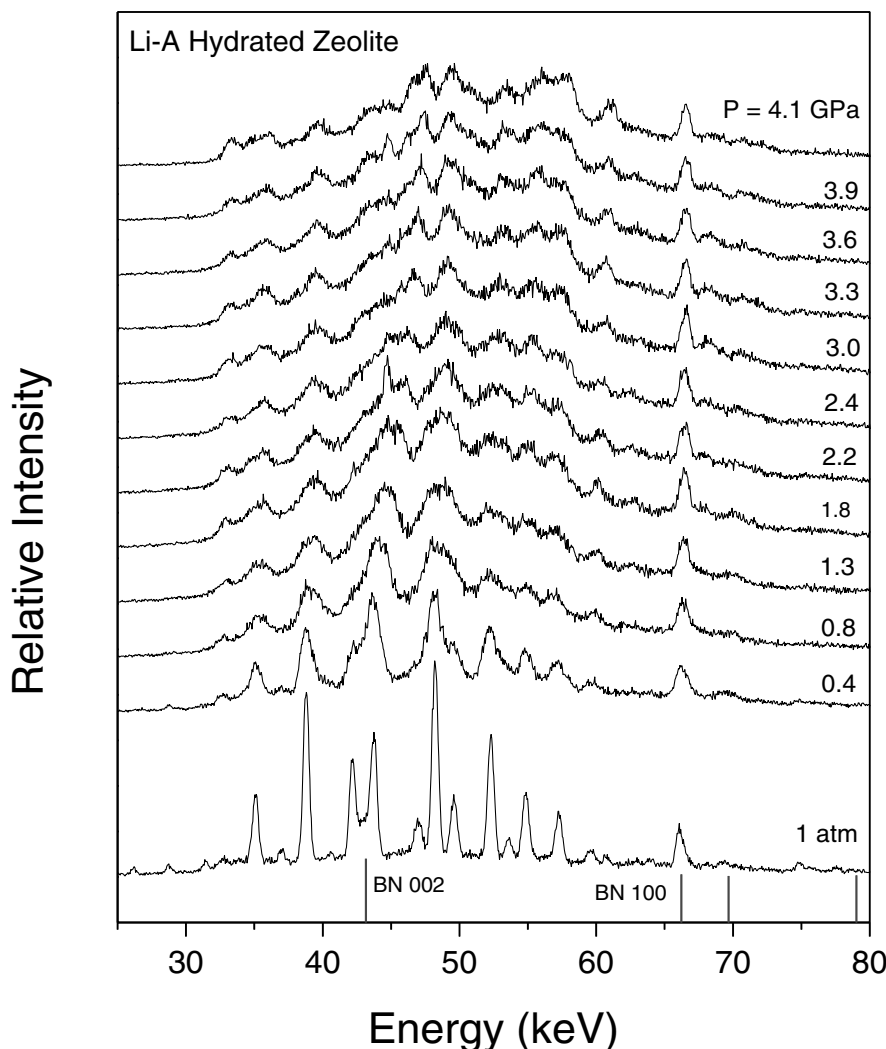


Fig. 1. Energy dispersive X-ray diffraction patterns for Li-A hydrated zeolite at pressures between 1 atm and 4.1 GPa. 1 atm hexagonal boron nitride diffraction peaks are shown as solid lines at the base of the figure.

ion-exchange methods. The purity and crystallinity of the samples were verified using X-ray diffraction (Philips PW1050 and Rigaku Geigerflex CN2029 powder diffractometer) with CuK_α and CoK_α radiation, and X-ray fluorescence (Philips PW1450). The zeolites had an atomic ratio of $\text{M}^+:\text{Al}:\text{Si}$ of 1:1:1, where $\text{M} = \text{Li}$ or Na . Samples were stored for 72 h, prior to loading into the high pressure cell, over a saturated solution of NH_4Cl to ensure a maximum degree of hydration. High pressure experiments were carried out at Argonne National Lab, using the Advanced Photon Source (APS) synchrotron. A 250 ton DIA-type high pressure apparatus installed on beamline 13 BM-D was used to generate the high pressures [14]. Energy dispersive X-ray diffraction (EDXRD) spectra were collected for 1000 s at each pressure interval with a Ge detector at a fixed 2θ angle of 4.95° . Both samples were contained in a cubic boron

nitride (BN) cup, and were separated by BN discs. Pyrophyllite was used as the pressure-transmitting medium. Pressure was measured with a NaCl pressure standard, included in two isolated layers in the BN cup, and the Decker equation of state [15]. All experiments were performed at room temperature.

3. Results and Discussion

Figs. 1 and 2 illustrate the EDXRD patterns for hydrated zeolite Li-A and Na-A, respectively, at several pressure intervals up to a maximum pressure of 4.1 GPa. Generally, it can be seen that as pressure increases, the sharp peaks that exist at ambient conditions in both the Li-A and Na-A samples quickly broaden, the intensity drastically decreases

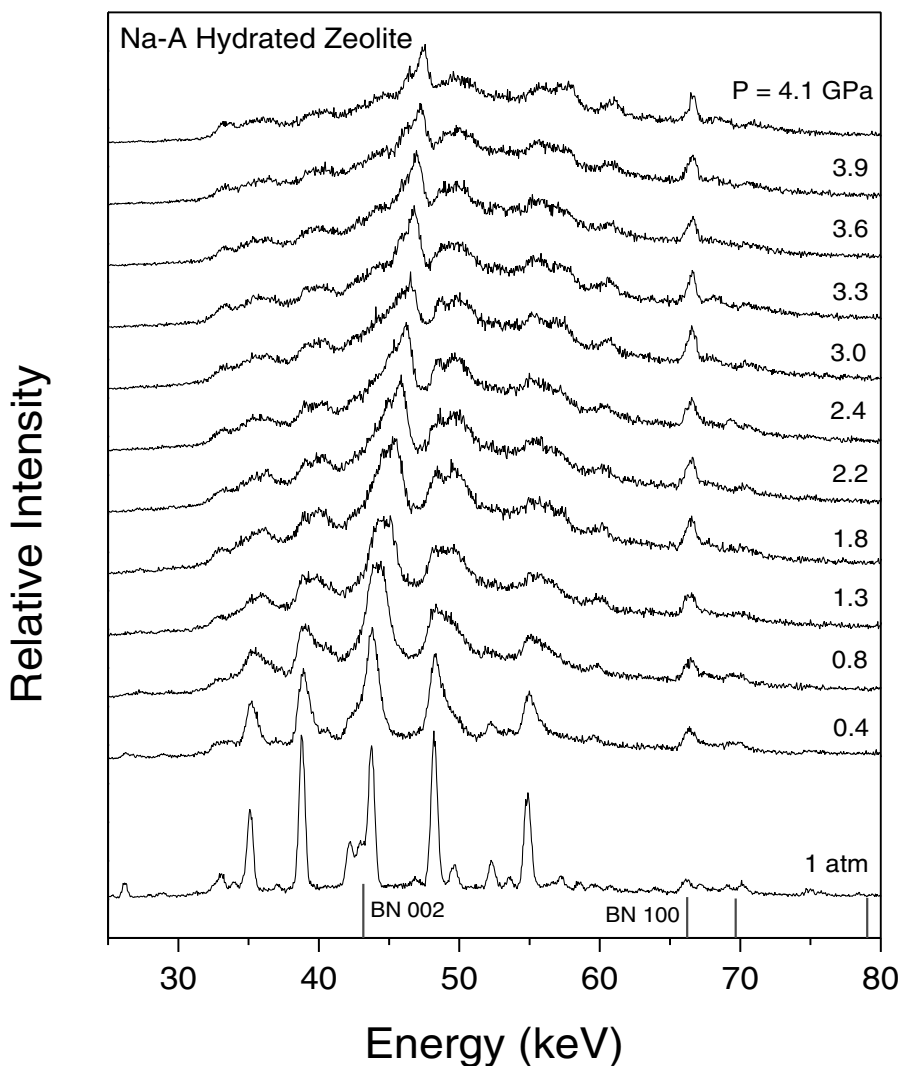


Fig. 2. Energy dispersive X-ray diffraction patterns for Na-A hydrated zeolite at pressures between 1 atm and 4.1 GPa. 1 atm hexagonal boron nitride diffraction peaks are shown as solid lines at the base of the figure.

and the peaks shift to higher energy. These changes are most prominent with increasing pressure up to approximately 2.2 GPa. Upon further compression the peaks continue to broaden and become less intense, however, the rate at which this occurs as pressure increases is greatly reduced. Within the EDXRD patterns for both zeolite Li-A and Na-A there are anomalous peaks at 66.0 keV, and visible in the Na-A patterns there is an anomalous peak ranging from 43–47.5 keV which persist until maximum pressure. These peaks were identified as the 100 and 002 peaks, respectively, from the hexagonal boron nitride material used to contain the zeolite sample in the experimental cell. We find a pressure dependence of the 002 peak and a pressure independence of the 100 peak, which is expected based on the anisotropic compression of hexagonal boron nitride [16].

The ambient XRD pattern for boron nitride is indicated by solid lines at the base of Figs. 1 and 2 [17].

3.1. Pressure-induced amorphization

The decrease in peak broadening and reduction in intensity observed for both zeolite Li-A and Na-A with increasing pressure is interpreted as gradual pressure-induced amorphization. To better illustrate peak shape and intensity enhanced views of the major peaks for zeolite Li-A and Na-A are plotted in Figs. 3 and 4, respectively, where the region contaminated by the BN has been removed. In these figures, the rapid decrease in peak intensity up to roughly 2.2 GPa can be seen more clearly. Peak 442 for the Li-A and Na-A samples decreases in intensity up to 1.3 GPa where it then

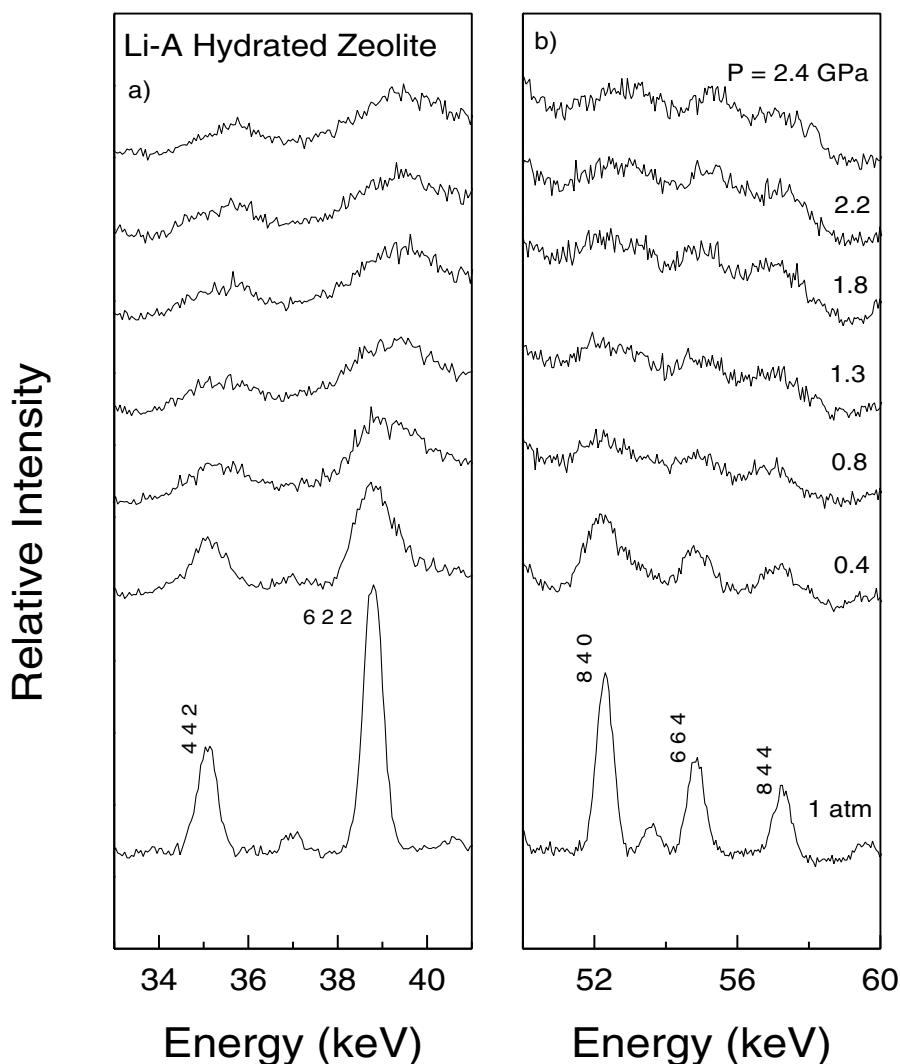


Fig. 3. Enlarged views of diffraction peaks for Li-A zeolite with the boron nitride signal removed. Intensities are plotted on the same scale as 1 atm patterns.

appears as a small hump. Similarly, peak 622 in each sample decreases in intensity until a maximum pressure of 1.8 GPa where it becomes a small bump. Again, this significant reduction of peak intensity signifies that the sample has undergone, to a large extent, long-range pressure-induced amorphization. The same behavior is observed in all other sample peaks. The 840, 664 and 844 peaks of zeolite Li-A, and the 664 peak of Na-A zeolite reduce in intensity and broaden very quickly and essentially flatten at 1.3 GPa while peak 644 of Na-A appears to persist until a maximum pressure of 2.2 GPa. Generally, it appears as though there is an abrupt decrease in peak intensity accompanied by peak broadening for both zeolites up to a maximum pressure of 2.2 GPa. Following this precipitous loss of order the zeolite becomes increasingly amorphous as pressure is further increased. At the maximum pressures achieved the crystal

structure appears to have lost most, if not all, of its long-range ordering. It is interesting to note that at 4.1 GPa the degree of pressure-induced amorphization appears to be greater in zeolite Na-A than Li-A. This can be seen in the EDXRD pattern for Li-A, Fig. 1, which has a less pronounced amorphous signature with slightly more peak structure than that of the Na-A sample at maximum pressure, as seen in Fig. 2. This could be due to the greater interaction of the Li^+ cation with the anion framework relative to that of the Na^+ cation. The greater charge density of the Li^+ cation binds it much more tightly to the anion framework, where it can then provide increased structural support under pressurization.

It should be mentioned that the scale at which amorphization is observed is only for the long-range. Strictly speaking,

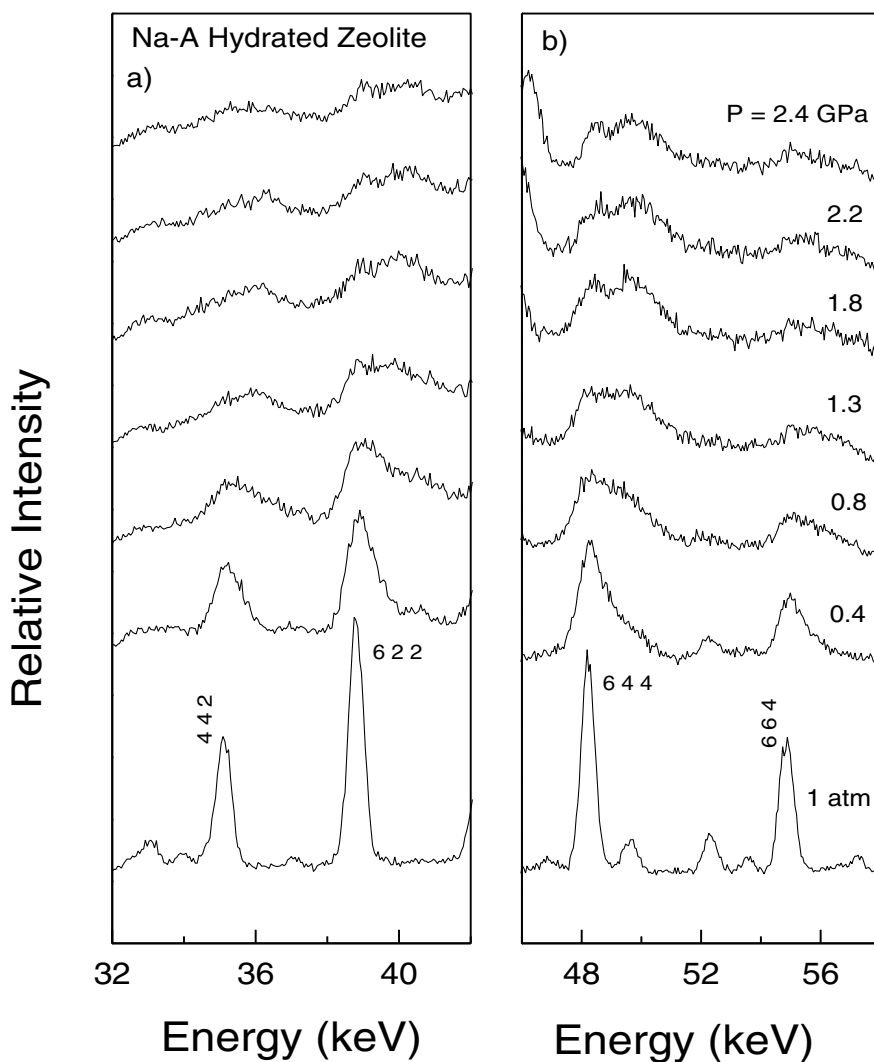


Fig. 4. Enlarged views of diffraction peaks for Na-A zeolite with the boron nitride signal removed. Intensities are plotted on the same scale as 1 atm patterns.

the observed amorphous material should be termed X-ray amorphous, referring to the loss of long-range correlation within the crystal lattice. Length scales which give rise to the X-ray diffraction signal indicate translational symmetry of the crystal on the order of 500–1000 Å [18]. Therefore, the amorphization observed through this study is a result of the length scale of the crystallinity reaching values less than the approximate threshold scale length of 500–1000 Å. One might interpret the reduction in X-ray peak intensity to be solely a result of small crystallite size (resulting from recrystallization in the quasi-hydrostatic, solid pressure medium, stress field), however, we present an argument against this interpretation in the next section. Having defined the scale of the observed amorphization the results of this study can be compared with other data on pressure-induced amorphization of zeolites and other materials derived from experi-

ments, such as IR spectroscopy, which are sensitive to short-range structural ordering.

In the IR spectroscopic study on zeolite Li-A, performed by Huang [3], a sharp reduction in intensity of the symmetric and asymmetric stretching vibrations was observed at about 1.8 GPa. Additionally, inter-tetrahedral T–O line broadening was observed and interpreted as the formation of an amorphous phase. The pressure at which the amorphous phase transformation was observed in Li-A by Huang coincides approximately with the pressure at which the intensity of the observed peaks from Li-A and Na-A in this study abruptly decrease in intensity. Based on this comparison, the loss of long-range ordering observed up to 1.3–2.2 GPa in this study could be due to the decrease of inter-tetrahedral separation, resulting in the amorphous long-range reorganization of the crystal lattice. Raman and

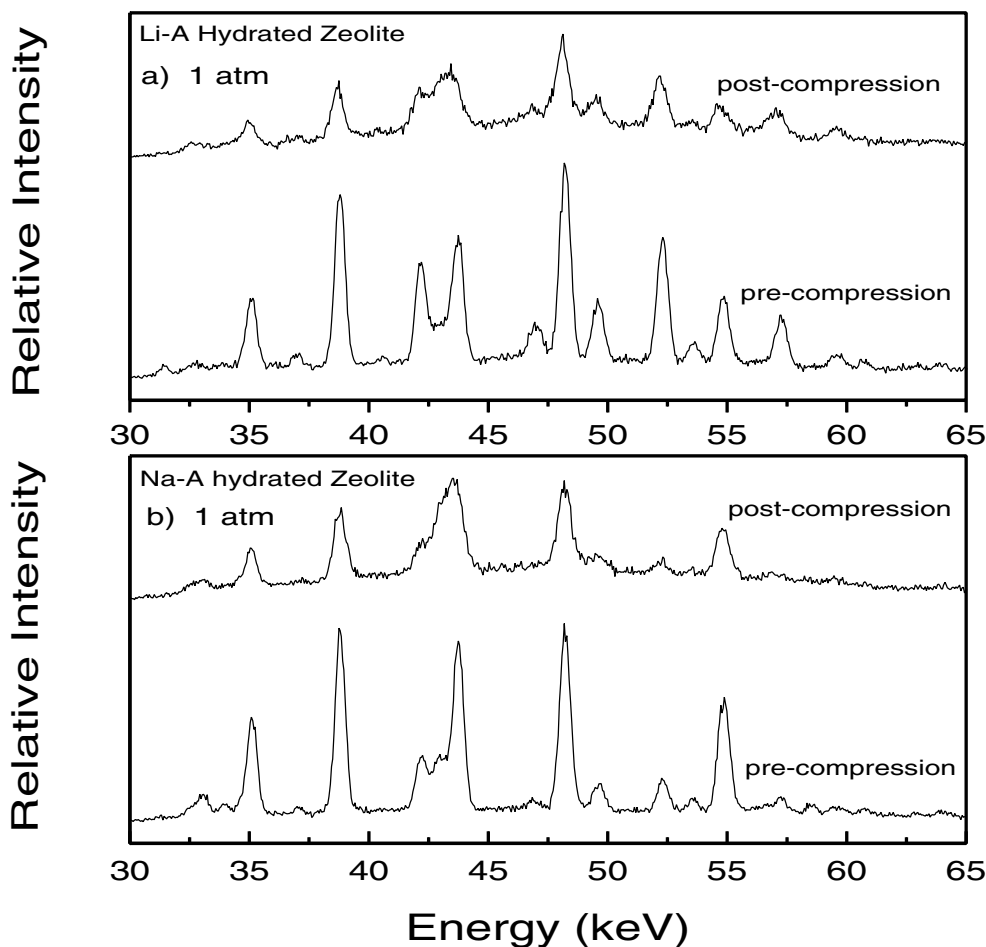


Fig. 5. (a) Diffraction patterns for Li-A zeolite at 1 atm for pre- and post-compression to 4.1 GPa. (b) Diffraction patterns for Na-A zeolite at 1 atm for pre- and post-compression to 4.1 GPa. Intensities are plotted on the same scale as the 1 atm patterns.

X-ray data [4], showed the progressive pressure-induced amorphization of microporous zeolites scolecite and mesolite above 8 GPa. Scolecite and mesolite crystallize in the orthorhombic system, and are similar to Linde A zeolites in that they are composed of extensive pore and channel networks [19]. This suggests, due to their microporous similarities, that the mechanism by which the amorphization takes place within scolecite and mesolite and the zeolites in this study could be related. The observed pressure-induced amorphization of scolecite and mesolite has been attributed to the increased spreading of the T–O–T angles caused by the progressive disruption of 4-member rings. This process has been observed in other materials [10,20,21] and could be the cause of pressure-induced amorphization of zeolite Li-A and Na-A. However, since the unit cell volume for scolecite is much smaller than that of Linde A and the pore and channels in the Linde A zeolites are much larger and more extensive, a comparison between the amorphization pressures is limited.

A study of the compressibility of Linde A zeolites as a

function of hydrostatic pressure medium was performed and a strong dependence of zeolite compressibility on the pressure transmitting medium found [22]. It was found that pressure-transmitting fluids of varying molecular size penetrate the microporous zeolite structure to various degrees depending on their relative size to that of the pores and channels. In turn, this gives rise to varying compressibility of the sample. Although, in the pressure range Hazen and Finger investigated, which is identical to the pressure range of this study, they reported no amorphization of the samples. Two possible explanations for the differences observed are the pressure transmitting media employed and the samples used. Firstly, penetration of the pressure-transmitting medium into the zeolite framework acts to buttress the zeolite framework under an applied load resulting in increased structural stability under pressure. Conversely, in our samples no fluid pressure-transmitting medium was used, and therefore there are no additional fluids within the pores and channels to structurally support the framework, thus resulting in our observation of pressure-induced

amorphization while previous studies observed none. When the diameter of the molecules of the fluid pressure-transmitting medium used was large enough to prevent penetration into the framework several discontinuities in the unit cell volume with increasing pressure were observed. Due to the ability of the experimental technique employed by Hazen and Finger to resolve small variation in the unit cell with pressure, the discontinuities they observed could be the manifestation, on smaller scales, of the long-range progressive amorphization of the sample. However, any comparison is speculative at best without detailed knowledge of their diffraction patterns. Secondly, the study examining the compressibility of zeolites also reports the results of single crystal measurements, whereas we have used polycrystalline samples. The differences in structural behavior under pressure could therefore be the result of differential stresses on individual crystals, which are a result of crystal–crystal interactions within the polycrystalline sample.

It is interesting to note the possible effects of a disruption or distortion of 4-member rings upon amorphization [4], on the mobility of ions in zeolites. From molecular dynamics (MD) simulations [23], the mobile cations, Li^+ and Na^+ , are located in the 6-, 8- and 4-member rings. The MD simulations show that ionic diffusion is dominated by ionic hopping between the 4- and 8-member rings. If the 4-member rings distort as pressure increases, the inter-site distance between 4- and 8-member rings, or more generally, the potential barrier to overcome between these sites, may reduce leading to greater ionic mobility. This was experimentally observed in measurements of ionic conduction at high pressure [5,13], and this may be the explanation for the anomalous pressure-induced increase in conduction at pressures up to ~ 2 GPa in Li-, Na- and K-A zeolites [24].

3.2. Structural memory

Observations have shown that some materials which undergo pressure-induced amorphization revert back to their crystalline state upon decompression [12,25,26]. Materials that undergo this phenomenon are said to have structural memory. Fig. 5a and b illustrate the EDXRD patterns for zeolite Li-A and Na-A before and after pressurization. The post-compression diffraction patterns were taken at 1 atm within the press immediately after unloading. From these figures, it is apparent that upon decompression Li-A and Na-A zeolites regain most of the long-range order which they lost during pressurization. All major peaks initially visible in the ambient diffraction patterns are regained after compression. The reduction in peak intensity observed in the post-compression sample could be due to the X-ray absorption of the extruded pyrophyllite gaskets which were present during the collection of the post-compression pattern while they were absent at ambient conditions. Therefore, zeolite Na-A and Li-A appear to have structural memory. The ability of the samples to revert back to their crystalline state after compression argues against the forma-

tion of small crystallites due to any quasi-hydrostaticity as described earlier. If the reduction in peak intensities was due to the formation of small crystallites, then the reappearance of a strong diffraction signal upon decompression would not be expected.

It has been shown that the presence of non-deformable units present within structurally microporous silicates is essential for the reversion back to the order state after pressure-induced amorphization has occurred [6]. These units act as templates about which the original crystal structure can be reformed. We suggest that at high pressure there exists some non-deformable units present within the zeolite sample which allow the reversion back to the ordered state. Some combination of the charge balancing cations, the water molecules present within the zeolite cages, and structural units of the original zeolite cage present at maximum pressure could act as templates upon which the original crystal structure would be reconstructed. The role-played by the charge balancing cations and water molecules during amorphization and recrystallization, and their structural importance at high pressure is not known. Follow up studies on dehydrated Linde A zeolites are planned to try and isolate the structural role of H_2O . In addition, remnant units of the original structure present at high pressures could act as vehicles through which recrystallization during the release of pressure would take place.

Acknowledgements

This work was performed at GeoSoilEnviroCARS (GSECARS), Sector 13, Advanced Photon Source at Argonne National Laboratory. GSECARS is supported by the National Science Foundation-Earth Sciences, Department of Energy-Geosciences, W.M. Keck Foundation and the United States Department of Agriculture. Use of the Advanced Photon Source was supported by the US Department of Energy, Basic Energy Sciences, Office of Energy Research, under contract No. W-31-109-Eng-38. We thank R. Tucker for the preparation of the high pressure cells and M. Rivers and S. Sutton for technical support. This work was supported by Natural Sciences and Engineering Research Council of Canada grants to R.A.S. and Y.H., and an NSF grant (EAR 9526634) to T.U.

References

- [1] R. Szostak, Handbook of Molecular Sieves, Van Nostrand Reinhold, New York, 1992.
- [2] H. van Bekkum, E.M. Flanigen, J.C. Jensen, Introduction to Zeolites Science and Practice, Elsevier Science, Amsterdam, 1991.
- [3] Y. Huang, J. Mater. Chem. 8 (4) (1998) 1067.
- [4] P. Gillet, J.-M. Malezieux, J.-P. Itie, Am. Mineral. 81 (1996) 651.
- [5] R.A. Secco, Y. Huang, J. Phys. Chem. Solids 60 (1999) 999.

- [6] J.S. Tse, D.D. Klug, J.A. Ripmeester, S. Desgreniers, K. Lagarec, *Nature* 369 (1994) 724.
- [7] O. Mishima, L.D. Calvert, E. Whalley, *Nature* 310 (1984) 393.
- [8] P. Richet, P. Gillet, *Eur. J. Mineral.* 9 (1997) 907.
- [9] S.M. Sharma, S.K. Sikka, *Prog. Mater. Sci.* 40 (1996) 1.
- [10] K.J. Kingma, C. Meade, R.J. Hemley, H.K. Mao, D.R. Veblen, *Science* 259 (1993) 666.
- [11] M. Madon, P. Gillet, C. Julien, G.D. Price, *Phys. Chem. Miner.* 18 (1991) 7.
- [12] Y. Fujii, M. Kowaka, A. Onodera, *J. Phys. C: Solid State Phys.* 18 (1985) 789.
- [13] M.D. Rutter, R.A. Secco, Y. Huang, submitted for publication.
- [14] Y. Wang, M. Rivers, S. Sutton, P. Eng, G. Shen, *Rev. High Press. Sci. Technol.* 7 (1998) 1490.
- [15] D.L. Decker, *J. Appl. Phys.* 42 (1971) 3239.
- [16] Y. Zhao, R.B. Von Dreele, D.J. Weidner, D. Schiferl, *High. Press. Res.* 15 (1997) 369.
- [17] T. Soma, A. Sawaoka, S. Saito, *Mater. Res. Bull.* 9 (1974) 755 (JCPDS 34-421).
- [18] S.A.T. Redfern, *Mineral. Mag.* 60 (1996) 493.
- [19] W.M. Meier, *Z. Kristallogr.* 113 (1960) 430.
- [20] G.H. Wolf, S. Wang, C.A. Herbst, D.J. Durben, W.F. Oliver, Z.C. Kang, K. Halvorson, in: Y. Syono, M. Manghnani (Eds.), *High Pressure Research: Application to Earth and Planetary Sciences*, Terrapub AGU, Washington, DC, 1992, p. 503.
- [21] R.M. Hazen, L.W. Finger, *Sci. Am.* 252 (1985) 110.
- [22] R.M. Hazen, L.W. Finger, *J. Appl. Phys.* 56 (6) (1984) 1838.
- [23] D.A. Faux, *J. Phys. Chem. B* 102 (1998) 10658.
- [24] R.A. Secco, M.D. Rutter, Y. Huang, *Russ. J. Tech. Phys.* (2000) (in press).
- [25] M.B. Kruger, R. Jeanloz, *Science* 249 (1990) 647.
- [26] J.S. Tse, D.D. Klug, *Science* 255 (1992) 1559.